# Wild avalanches and mild fluctuations during filiform corrosion of Mg in NaCl solution

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The filiform corrosion of Mg in NaCl solution was characterized by acoustic emission spectroscopy, measurements of the free-corrosion potential, and optical observations under *in situ* conditions. Three stages of corrosion were identified: an incubation period, localized attack, and filament propagation. The corrosion mechanisms include the Mg dissolution, the breakdown of hydroxide/oxide surface films, and the burst of gas bubbles. Localized attack and filament propagation are distinguished by a gradual transition from correlated avalanches (wild events) to predominantly stochastic processes (mild events), which still contain some weak avalanche signals. Our approach provides a way to monitor corrosion under *in situ* conditions.

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### I. INTRODUCTION

Avalanches commonly relate to microstructural changes during deformation and failure of materials [1,2]. Such changes are induced by external stress, electric or magnetic fields, or thermal stress [3–7]. Avalanches are ubiquitous in externally driven processes; they include flux penetration in type II superconductors [8], Barkhausen noise due to the domain distribution in ferromagnets [9], the propagation velocity of  $Mn_{12}Ac$  (a single-molecule magnets material) in pulsed magnetic fields [10], crack and twinning during compression of martensitic porous Ti-Ni [11], dislocation slip in crystalline and amorphous materials [12–19], internal and external friction in the glass-hydrogel interface [20], and twin reconfiguration under an electric field in  $SrTiO_3$  and  $BaTiO_3$  [21–24]. The sudden bursts of chemical activity at the interface between metals and liquid electrolytes were related by Claycomb et al. [25,26] to avalanche-like behavior of chemical reactions. They measured the related time-dependent chemomagnetic fields by superconducting quantum interference device.

The majority of electrochemical systems involve intricate dynamics including anodic dissolution, cathodic deposition, and electrocatalytic activation, which are associated with corrosion of various metals. Such electrochemical reactions have attracted significant attention [27]. It is the purpose of this paper to show that similar avalanches exist in electrochemical reactions caused by metal corrosion.

Avalanches compete with another type of uncorrelated structural changes which are stochastic fluctuations [28]. Weiss [29–32] introduced the terms "wild" and "mild" for

these events and the transition from wild to mild events was previously found in metals [29-31,33,34], ice [32], and medical materials like kidney stones [35]. Acoustic emission (AE) signals from jerky flow in AlMgScZr were reported as results from collective dynamics of dislocations which gives rise to serrated deformation curves and a complex evolution of the strain heterogeneity by Ref. [36]. The acoustic emission processes obeyed power-law scaling which indicated avalanche-like dynamics. The scaling exponents displayed strong dependences on the strain and the strain rate and were described as evidence for a competition between the phenomena of synchronization and randomization of dislocation avalanches. We will follow similar arguments and report randomized mild events and collective wild events. Lebedkina et al. [36] used the strain rate in their experiments to investigate the strain dependence of the avalanche dynamics. We will show in this paper that the similar transitions occur during the corrosion of Mg in NaCl solution as a test case for further investigations.

The statistical properties of microstructural changes are well observed by AE spectroscopy. It is commonly used for the study of metal corrosion due to its high sensitivity, nondestructiveness, and its capability of in situ monitoring, e.g., during materials applications. AE signals are elastic waves emitted by sudden structural changes; they propagate inside the material and are detected by an AE sensor attached to the sample surface [37]. AE spectroscopy is widely used to monitor and characterize mechanical fatigue and progressive failure in bridges [38], concrete blocks [39], stainless-steel constructions [40], and fiber composites [41]. As statistical analysis allowed the identification of collapse mechanisms in geological hazard assessment [42], a full statistical analysis of AE signals has become the gold standard in rock mechanics (sandstone [42], coal [43]) and metallic alloys [40], which led to a comprehensive understanding of the related avalanche processes.

Previous AE work on corrosion mostly focused on the identification of AE signals without statistical analysis [44–50]. AE events during pitting corrosion in passive alloys have been reported, including the rupture of salt films, the

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FIG. 1. Experiment arrangement with *in situ* acoustic emission (AE), free-corrosion potential ( $E_{corr}$ ), and optical microscopy (OM) measurements. (1) corrosion cell, (2) sample, (3) AE sensor, (4) AE preamplifier, (5) AE acquisition computer, (6) optical microscopy, (7) optical microscopy computer, (8) counterelectrode, (9) reference electrode, and (10) potentiostat acquisition computer.

deposition of corrosion products [44], transpassive dissolution [45], the perturbation of electrolytes [46], and the rupture of hydrogen bubbles [47]. AE signals are also generated during corrosion cracking in passive alloys, including crack propagation [48], ligaments tearing, and plastic deformation of crack tips [49]. For active alloys, AE was used to identify the ion exchange, rupture of the protective film, and pit growth [50].

In this paper we report avalanches of AE signals during the corrosion process of Mg by 0.1 M NaCl solutions. We find a gradual transition from correlated avalanches (wild events) to stochastic processes (mild events) of AE signals, indicating that the corrosion mechanism changes from localized attack to filament propagation. Our approach not only proves the existence of avalanches during electrochemical reactions caused by metal corrosion, but also provides a way to monitor corrosion under *in situ* conditions.

### **II. EXPERIMENT**

#### A. Materials and experiment arrangements

As-cast Mg used in this study contained the following impurities: Al (0.0002 wt.%), Zn (0.004 wt.%), Fe (0.006 wt.%), and Cr (0.004 wt.%). The samples were cut into cuboids of 10 mm  $\times$  10 mm  $\times$  12 mm, ground with 2000-grit SiC paper, polished with 0.5- $\mu$ m diamond paste, and cleaned in an ultrasonic bath using ethanol.

Figure 1 shows the experiment arrangement for the *in situ* monitoring of AE, free-corrosion potential ( $E_{corr}$ ), and optical microscope (OM) during the corrosion of Mg. The sample was cast in epoxy with one end attached to a piezoelectric AE sensor; the opposite surface of 1 cm<sup>2</sup> was exposed to the corroding solution. The sample was placed horizontally at the bottom of the cell and immersed in the test solution.  $E_{corr}$  was monitored at an acquisition rate of 1 Hz using a Versa STAT potentiostat. A saturated calomel electrode (SCE) (all potentials in this paper are referred to this standard) and a Pt plate were used as the reference and counter electrodes. The OM (Zeiss Axiolab 5) was placed upright over the solution to monitor the morphology change during corrosion.

Scanning electron microscope (SEM, Hitachi SU8230) was used to characterize the surface corrosion morphologies and the cross-sectional morphologies at different stages. Once removed from the test solution, the samples were rinsed

with ethanol, dried using a stream of air, and placed in a vacuum container. The cross-sectional samples were cast in resin, polished with 0.5-µm diamond paste, cleaned in an ultrasonic bath using ethanol, and then placed in a vacuum container. The total time to transport the corroded sample from the vacuum container into the chamber of the SEM instrument was about 15 min. The surface morphologies were obtained by the secondary electron mode with an accelerating voltage of 3 kV. The cross-sectional morphologies were obtained by low-angle backscattered electron imaging with an accelerating voltage of 5 kV.

### **B.** AE measurements

AE signals were measured during the corrosion process and converted into electrical signals by the attached piezoelectric sensor (Vallen-Systeme GmbH) with a frequency range of 200-800 kHz. The recording signals were first preamplified by 49 dB and then transferred for waveform analysis using an AMSY-6 AE-measurement system with a frequency range of 95–850 kHz and a sampling rate of 20 MHz. The energy of an AE event is measured by the area under the signal envelope. It is then calibrated by the AE equipment to absolute values; the energy unit is attojoule (aJ). To calibrate and exclude background noise, we measured a polyvinyl chloride sample using the same experiment arrangement. As the polyvinyl chloride sample does not react with the solution, the collected AE signals represent pure background noise. The probability distribution function of AE energies of the background noise follows a log-normal distribution. The measurable noise energy is below 0.05 aJ, indicating that events with energies above 0.05 aJ relate to corrosion processes and not to background noise.

### C. Statistics analysis

The energies of the AE signals were analyzed using their probability distribution functions (PDFs). PDFs are defined as the number of events in a given energy range per bin width divided by the total number of events. In wild avalanches they are power-law distributed:

$$P(E) \sim E^{-\varepsilon},\tag{1}$$

where  $\varepsilon$  is the energy exponent [51]. The exponent  $\varepsilon$  is determined by the slope of a negative linear relationship on a log-log scale. The power law implies that the process is scale invariant. However, the power law P(E) often contains some cutoff at low or high energies:

$$P(E) \sim E^{-\varepsilon} \left( 1 - e^{-(E/s_0)^{\nu}} \right), \tag{2}$$

where  $s_0$  and v are constants, which are not investigated in this study. Alternatively, P(E) follows a gamma distribution if the process is, at least partially, mild and not scale invariant. The gamma distribution is parametrized by a shape parameter  $\alpha$  and a rate parameter  $\beta$ :

$$P(E) \sim \frac{\beta^{\alpha}}{\Gamma(\alpha)} E^{\alpha-1} e^{-\beta E},$$
(3)

where  $\Gamma(\alpha)$  is the gamma function [52]. The parameters of Gamma distributions were fitted by maximum likelihood



FIG. 2. (a) Distribution of peak frequencies vs energy for AE signals of Mg immersed in 0.1 M NaCl solution. Typical waveforms of (b) Mg dissolution (cluster 1), (c) film breakdown (cluster 2), and (d) bubble bursts (cluster 3) are shown in (b)–(d).

estimates:

$$\ln \alpha - \psi (\alpha) = \ln \left( \bar{E} \right) - \frac{1}{N} \sum \ln (E), \qquad (4)$$

where  $\beta = \frac{\alpha}{\bar{E}}$ ,  $\bar{E}$  is the sample mean for the dataset  $E_1, E_2, \ldots E_N$ , and  $\psi(\alpha)$  is the digamma function. The likelihood is the probability density function viewed as a function of the parameters.

## **III. RESULTS**

### A. AE signals during the corrosion process

Figure 2(a) shows peak frequencies as function of the peak energy during the corrosion experiment. Three frequency clusters are identified, as shown in green, blue, and orange. The frequency ranges for the three clusters are 200–250, 280–353, and 380–800 kHz, respectively. Figures 2(b)–2(d) show the typical waveforms of the three clusters. The typical waveforms of cluster 1 and 2 possess high amplitudes and long durations, while the rise times of cluster 1 are longer than cluster 2. The typical waveforms of cluster 3 exhibit low amplitudes, and short durations and rise times.

Figure 3(a) shows the variation of free-corrosion potential ( $E_{\rm corr}$ ), AE signals, and the cumulative AE during immersion. The AE activity is highly nonuniform [53] and three stages are identified. In stage I (0–1232 s), the  $E_{\rm corr}$  increases rapidly from -1.92 to -1.55 V<sub>SCE</sub>, and no AE signal is detected. Such behavior is similar to that of passive alloys, indicating the formation of a protective film on the surface. In stage II (1232–1903 s),  $E_{\rm corr}$  first decreases at 1232 s [arrow in

Fig. 3(a)] corresponding to the initiation of localized attack [54]. Simultaneously, AE signals commence and the number of cumulative events increases. The rate of AE events in stage



FIG. 3. (a) Free-corrosion potential (black line), AE signals (purple peaks), and cumulative events (red line) for Mg immersed in 0.1 M NaCl solution. Corrosion process includes three stages: incubation period in stage I, localized attack in stage II, and filament propagation in stage III. AE signals, average energy, and cumulative events for (b) Mg dissolution, (c) film breakdown, and (d) bubble burst.



FIG. 4. *In situ* optical microscopy images of Mg immersed in 0.1 M NaCl solution. Images (a), (b), and (c) correspond to points A, B, and C (A: 0 s, B: 1300 s, and C: 2610 s) in Fig. 3(a). (d)–(f) Cross-sectional and (g)–(l) surface SEM images of Mg after immersion 600 s in stage I, 1500 s in stage II, and 3000 s in stage III in 0.1 M NaCl at room temperature.

II is about 1.7 hits per second. In stage III (1903–3000 s), the  $E_{\rm corr}$  slightly decreases to -1.57 V<sub>SCE</sub>. The increase of the cumulative AE events becomes stronger, and the AE activity increases to 4.3 hits per second. Figures 3(b)–3(d) show the average energy of clusters 1–3, respectively. The average energies are calculated as sum of the AE energies divided by the number of AE signals every 6 s. Stage I shows no signals, stage II shows sparse signals with higher intensities, while stage III shows a high density of AE signals.

## B. In situ and ex situ observations during corrosion process

Figures 4(a)-4(c) show the *in situ* optical images of Mg immersed in 0.1 M NaCl solution. The images (a)–(c) correspond to points A–C in Fig. 3(a). Figure 4(a) shows the original surface of Mg. Figure 4(b) shows black circles of hydrogen bubbles which grow at the metal/solution interface. Mg undergoes filiform corrosion which was initiated by localized attack, and filament propagation which is characterized by growth of the dark areas in Fig. 4(c).

*Ex situ* SEM images are shown in Figs. 4(d)-4(1). In stage I, the cross-sectional and surface morphologies show that the Mg matrix in this stage is intact, as shown in Figs. 4(d), 4(g), and 4(j). In stage II, Figs. 4(e) and 4(h) show the initiation of localized corrosion as indicated by the dark red arrows. Figure 4(k) shows the occurrence of film breakdown as indicated by the yellow arrow. In stage III the unique behavior of pure Mg undergoes filiform corrosion [Fig. 4(c)]. The corroded areas rapidly propagate on the Mg surface [Figs. 4(f), 4(i), and 4(1)]. In short, the corrosion mechanisms fall into three time regimes, namely stage I with the formation of a protective surface layer, stage II with localized attack, and stage III with filament propagation.

## **IV. DISCUSSION**

### A. Correlation between AE signals and corrosion process

To differentiate between various AE signals during the corrosion process, it is necessary to identify the corresponding AE sources based on peak frequencies and cumulative AE



FIG. 5. Probability distribution function (PDF) of energy for (a)–(c) localized attack (stage II), (d)–(f) filament propagation (stage III) of Mg dissolution, film breakdown, and bubble burst, respectively. Cutoff power law follows  $P(E) \sim E^{-\varepsilon} (1 - e^{-(E/s_0)^{\nu}})$ . Power law follows  $P(E) \sim E^{-\varepsilon}$  for high energies and Gamma distribution follows  $P(E) \sim \frac{\beta^{\alpha}}{\Gamma(\alpha)} E^{\alpha-1} e^{-\beta E}$  for energies below ~0.7 aJ.

events, as shown in Fig. 2(a) and Figs. 3(b)-3(d). AE events are observed only in stages II and III. The onset of stage II is easily detectable by AE. In stages II and III, we distinguish between three corrosion mechanisms by comparison of  $E_{corr}$ , SEM, and optical observations. These are the Mg dissolution, the film breakdown, and the bubble bursts.

In stage I, no AE signals were detected. Therefore, neither the growth of hydrogen bubble nor the gradual formation of the plateletlike  $Mg(OH)_2$  film [Fig. 4(j)] generate AE signals. In stage II, when the bubbles collapse, they cause dissipation of energy in the water [55]. Husin *et al.* [56] and Jirarungsatian and Prateepasen [57] reported that bubble burst can generate AE signals and the burst frequency is determined by the bubble size. The minimum burst frequency becomes [55,57,58]

$$v_b = \frac{1}{\pi D_{\text{max}}} \sqrt{\frac{3\gamma P_0}{\rho_0}}.$$
 (5)

The bubbles are assumed to be filled with an ideal gas where the specific heat for the gas is  $\gamma = 1.4 \text{ J/(kg K)}$ ; the static pressure in the fluid is  $P_0 = 3.110 \times 10^7 \text{ kg/m}^2$ . A Newtonian fluid with constant density  $\rho_0 = 1000 \text{ kg/m}^3$ [57,58] is assumed and  $D_{\text{max}}$  is the maximum diameter of a stable bubble. In situ optical images on the bubbles [e.g., Fig. 4(b)] show that the diameter of bubbles is approximately  $175 \sim 257 \mu \text{m}$ , indicating the burst frequency for the vast majority of bubbles ranges from 447 ~ 656 kHz. In addition, a few bubbles with a maximum diameter of ~ 300  $\mu \text{m}$  during the corrosion process indicate that the burst frequency should be higher than 380 kHz, which is consistent with the frequency distribution of the green cluster in Fig. 2(a). We therefore conclude that the green cluster 3 in Figs. 2(a) and 3(d) (380–800 kHz) correlates with bubble bursts. In stage II, the first drop of  $E_{\rm corr}$  at 1232 s is attributed to the local attack originated from the local breakdown of the film, resulting in the active dissolution of Mg. The film breakdown [57,59] and the active dissolution of metal lead to AE signals [60]. Figures 3(b)–3(d) show that the cumulative events of orange clusters and green clusters (bubble bursts) have similar trends, while the blue clusters display rare signals in stage II. As the hydrogen bubble is generated by the dissolution of Mg, the dissolution rate of Mg is positively correlated with the bubble-burst rate. Therefore, the orange cluster 1 in Figs. 2(a) and 3(b) stems from Mg dissolution.

In addition, the burst signals are associated with a possible rupturing process, leading to small holes on the sample surface [61]. Thus, the burst signals of blue cluster 2 in Figs. 2(c) and 3(c) can be attributed to the breakdown of the protective film on the Mg surface.

### B. Transition from wild-to-mild events during filiform corrosion

Figures 5(a)–5(f) summarize the energy PDFs for different corrosion process. Only stage II [Figs. 5(a)–5(c)] and stage III [Figs. 5(d)–5(f)] can be seen because AE is absent in stage I. We distinguish between the three mechanisms seen optically and by SEM, namely the Mg dissolution, the film breakdown, and bubble bursts. For stage II, the PDFs for Mg dissolution and film breakdown events follow a cutoff power-law distribution. The energy exponents are  $\varepsilon = 2.78$  and  $\varepsilon = 2.98$ . A stochastic regime occurs below 0.23 aJ. The energy PDF analysis of bubble-burst events shows that the Gamma distribution is now dominant over the power law. Only at large energy (> 0.4 aJ) does the PDF show the power-law tails with approximate exponents  $\varepsilon = 2.68$ , as shown in Fig. 5(c).

TABLE I. Parameters for stage II (localized attack), stage III (filament propagation) of Mg dissolution, film breakdown, and bubble burst, respectively.

	Stage	ε	au'	x	$\tau'$ -1	$(\varepsilon - 1)x$
Mg dissolution	Π	2.78	4.76	2.18	3.76	3.88
	III	3.50	5.58	2.06	4.58	5.15
Film breakdown	Π	2.98	5.72	2.10	4.72	4.16
	III	3.17		1.96		4.25
Bubble burst	II	2.68	3.36	1.92	2.36	3.22
	III	1.92	2.71	1.97	1.71	1.81

Compared with stage II, the PDF analysis of Mg dissolution and film breakdown events shows that the Gamma distribution is now dominant over the power law [Figs. 5(d) and 5(e)]. The stochastic regions extended to 0.7 aJ in both cases, and the power-law tails are only seen at higher energies (>0.7 aJ). Taking into account the relatively large errors in the determination of the energy exponents, we find no tangible difference of the power-law exponents between stages II and III ( $\varepsilon = 2.7-3.5$ ). In addition, the bubble-burst events also show that the Gamma distribution region extends to a higher energy (from 0.4 to 0.9 aJ) in stage III. These results indicate that there is a transition from correlated avalanches (wild) to stochastic processes (mild) of AE signals from stage II to stage III.

[See Figures 8(a)-8(f) in the Appendix which summarize the amplitude PDFs for different corrosion process.] The power-law scaling  $P(A) \sim A^{-\tau'}$  is well seen in stage II and III for Mg dissolution and bubble burst. The power-law region decreases for the other scenarios, where power-law amplitude scaling is still visible in stage II for film breakdown events. The above results indicate that transitions from wild-to-mild events can be obtained from the amplitude scaling although the energy scaling is more reliable. [See Figs. 9(a)-9(f), which show the power-law scaling between energy and amplitude  $(E \sim A^x)$ , where the exponent x is close to 2.] Table I lists a summary of estimates for the energy exponents, amplitude exponents, and the E(A) correlation. The relationship  $\tau'-1 = (\varepsilon - 1)x$  is approximately fulfilled. We note that it is not possible to obtain reliable data for the avalanche durations which are between 2 and 10 µs. In addition, we note that in our experiments the detector is much smaller than the sample and we do not expect any dependence on the sample size [22].

To quantitatively describe this wild-to-mild transition, we calculated the degree of wildness (W), which is defined as [33]

$$W = \frac{\sum_{E > E_{\min}} E}{\sum_{\text{total}} E},\tag{6}$$

where  $E_{\min}$  is the threshold distinguishing between wild and mild [34]. Specifically, the threshold is determined by the minimum energy of the power-law regime.

In stage II, W = 0.90 and W = 0.87 for the AE signals of Mg dissolution and film breakdown, respectively, while the wildness for the AE signals of bubble burst shows a small value of 0.20, as shown in Fig. 6. In stage III, the wildness for all three subsets of AE signals is small (W < 0.09), e.g., W = 0.09 for Mg dissolution and W = 0.07 for film breakdown.



FIG. 6. Degree of wildness (W) for localized attack (stage II) and filament propagation (stage III) of Mg dissolution, film breakdown, and bubble burst.

As the corrosion mechanism changes from localized attack to filament propagation (shown in Fig. 4), Fig. 6 shows that there is a transition from a wild regime to a predominantly mild regime when the localized attack transforms to filament propagation.

The results from AE spectroscopy can hence be summarized as follows: wild avalanches generate correlated AE signals, which are power-law distributed. These avalanches are placed in the energy spectrum at high energies. The lowenergy cutoff is 0.23 aJ in stage II and localized peaks appear at lower energies. In stage III, we find that the localized peak is much stronger and extends to 0.70 aJ. The powerlaw exponents seem to increase with increasing localization, although this effect is small and may reflect a spurious reading of the exponents. The majority of power-law exponents are constrained between 2.78 and 3.50, whereby the lower exponents have smaller uncertainties than the larger exponents. The exponents are much higher than those predicted by mean-field theory, namely 1.66, which dominate most AE measurements of microstructural changes in metals and alloys [51,53].

Large exponents may reflect multiple pathways for avalanche mechanisms. Simple collapse mechanisms typically assume the mean-field values with  $\varepsilon = 1.33$  and  $\varepsilon =$ 1.66 [51]. This is not the case in our corrosion experiments. High exponents were previously observed in some microstructural changes with complex pathways [62]. A similar scenario can be evoked here. High-energy AE signals relate to spatially correlated processes like the removal of parts of the protective layer or the forward progression of the corrosion front. In these cases, any small local perturbation will trigger other local events. All these events happen over a very short time interval and form one avalanche. These avalanches are hence wild and can be described classically by power-law distributions. The high exponent is then ascribed to the complex or perhaps glassy correlation between the local events [63,64].

In contrast to these correlated events, the localized events show the hallmarks of mild avalanches or even uncorrelated, stochastic movements. This relates the energies below the cutoff. A typical example would be a single bubble on a



FIG. 7. Schematic diagram of (a), (b) cross-sectional and (c), (d) surface morphologies in stage II (localized attack) and stage III (filament propagation) occurring on Mg.

surface. The burst will generate a weak AE signal. Bubbles may not interact and the AE spectrum consists of many signals which are distributed over a small energy interval which is determined by the burst energy of a bubble. If, on the other hand, the bubbles are closely spaced, they will elastically interact, either by the deformation of the metal surface or via the surrounding liquid. In this case, a bursting bubble will initiate other bubbles to burst, and avalanches will develop. These avalanches are then scale invariant and generate high-energy signals by the almost simultaneous motion of all bubbles involved in the bubble bursts.

# C. Correlation between corrosion mechanisms and the wild-to-mild transition of AE signals

In stage I, the Mg matrix does not corrode immediately when it is immersed in the solution because of the air-formed



FIG. 8. Energy vs amplitude correlations for (a)–(c) localized attack (stage II), (d)–(f) filament propagation (stage III) of Mg dissolution, film breakdown, and bubble burst, respectively. Correlation between energy (*E*) and maximum amplitude (*A*) follow approximately  $E \sim A^x$ .



FIG. 9. PDF of amplitude (*A*) for (a)–(c) localized attack (stage II), and (d)–(f) filament propagation (stage III) for Mg dissolution, film breakdown, and bubble burst. Power laws follow  $P(A) \sim A^{-\tau'}$  for high amplitude, where  $\tau'$  is amplitude exponent.

oxide film (principally consisting of MgO) covering the Mg surface. MgO is not stable in aqueous solution, and reacts with water and gradually transforms into Mg(OH)<sub>2</sub>. Additionally, as the Pilling-Bedworth ratio for MgO/Mg is 0.81 [65], the MgO film cannot cover the entire surface and the bare Mg matrix is exposed in local areas. Hydrogen bubbles grow at the metal/solution interface. Mg(OH)<sub>2</sub> forms additionally in the exposed areas of the Mg matrix [66]. This coverage leads to inhibitory effects [Figs. 4(g) and 4(j)], and no AE signals are detected in stage I.

In stage II,  $Cl^-$  increasingly destroys the Mg(OH)<sub>2</sub> protective layer, leading to the film breakdown and the occurrence of localized attacks. The initiation of localized corrosion is regions of intense local anodic activity. Subsequently, anodic activities initiate rapid deactivation and the development of a strong local cathode [54,67]. The intense local anodic and local cathode in the early stage of filiform corrosion show peak current densities [68], which correlate with wild avalanches in stage II.

In stage III, filament propagation occurs on the Mg surface. The filiform corrosion of Mg is governed by a "differential electrocatalytic" mechanism [68], involving anodic Mg dissolution (Mg  $\rightarrow$  Mg<sup>2+</sup> + 2e<sup>-</sup>) at the leading edge of the corrosion front and galvanically coupling with hydrogen evolution (2H<sub>2</sub>O + 2e<sup>-</sup>  $\rightarrow$  H<sub>2</sub> + 2OH<sup>-</sup>) on a cathodically activated corroded region [68,69]. Such a mechanism is under cathodic control [54,70], and can be limited by the following factors. First, the elevated local pH is generated by cathodic hydrogen evolution, which protects the corroded regions from further anodic dissolution [54]. Specifically, the solubility of Mg(OH)<sub>2</sub> in the vicinity of the local cathode is reduced by a factor of 10<sup>12</sup>, causing the anodic activity to switch off and limiting the depth of the observed attack [71]. Another important factor is the ohmic constraints [54,72]. As Cl<sup>-</sup> are covered at the corrosion front [73,74], the dilute NaCl(aq) electrolyte shows higher resistivity [72], and thus lower current density of local cathodes [68,72], which is insufficient to sustain the uniform anode at the perimeter of a circular corroded area [67]. The electrochemical reactions tend to occur at random points, thus exhibiting more stochastic behavior of AE signals in stage III.

A schematic diagram representing the mechanism of localized attack and filament propagation on Mg is proposed in Fig. 7.

### V. CONCLUSION

1. Three AE mechanisms are identified, namely Mg dissolution, film breakdown, and bubble burst.

2. Three corrosion stages of Mg are observed, including an incubation period (stage I), localized attack (stage II), and filament propagation (stage III). AE events were observed only in stages II and III.

3. Localized attack and filament propagation are distinguished by the gradual transition from avalanches dominant (wild) to more stochastic (mild) events. The statistical analysis allows to analyze dynamic corrosion behavior under *in situ* conditions.

4. The large uncertainties of the measured avalanche parameters are due to the scarcity of the data points. Nevertheless, we have shown that it is possible to characterize corrosion processes via mild and wild fluctuations. Future work is highly desirable.

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# APPENDIX: DISTRIBUTIONS OF AMPLITUDE SCALING AND ITS RELATIONSHIP WITH ENERGY SCALING

The power-law region (Fig. 5) has energy exponents  $\varepsilon$  between 2.7 and 3.5. The exponents *x* for correlation between energy and amplitudes are shown in Fig. 8. They range from 1.92 to 2.18, which is close to the value 2 which is expected in a simple model [2]. The amplitudes are assumed to be directly related to the sizes as derived in Ref. [24]. The amplitude scaling (Fig. 9) shows power laws with exponents  $\tau'$  between

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2.7 and 5.7. The power-law region for amplitudes is very small in stage II and stage III for all Mg dissolution, film breakdown, and bubble burst.

The power-law region of the amplitude scaling is very small in stage II and stage III for all three mechanisms. A summary of rough estimates of the energy exponents, amplitude exponents, E(A) correlation, and the relationship between them are shown in Table I. We observe that the relationship  $\tau'-1 = (\varepsilon-1)x$  is only approximately valid. This is due to the very sparse datasets with large data scatter.

We note that it is not possible to obtain reasonable data for the avalanche durations which are between 2 and 10  $\mu$ s. This interval is too small to retract reliable exponents.

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